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INVESTIGACIÓN

Interactions in interesterified palm and palm kernel oils mixtures. I-Solid fat content and consistency

By **Renato Grimaldi**[1*], **Lireny Aparecida Guaraldo Gonçalves**[1], **Luiz Antonio Gioielli**[2] and **Ilka S. Simões**[2]

[1]Laboratório de Óleos e Gorduras – Faculdade de Engenharia de Alimentos (FEA) – Universidade Estadual de Campinas (UNICAMP), Caixa Postal 6091, CEP 13081-970, Campinas , SP, Brazil. E-mail: grimaldi@fea.unicamp.br
[2]Faculdade de Ciências Farmacêuticas – Universidade de São Paulo (USP). E-mail: lagio@usp.br

RESUMEN

Interacciones entre mezclas de aceites de palma y palmiste interesterificados. I–Contenido de grasa solida y consistencia.

Se interesterificaron, en el laboratorio, mezclas de aceite de palma (PO) y aceite de palmiste (PKO): 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 y 0/100 en condiciones predefinidas (0.4% metóxido de sodio, 20 minutos, 100°C). Las catorce muestras fueron caracterizadas antes y después de la interesterificación por su contenido de grasa sólida (SFC) y su consistencia. Los resultados mostraron la presencia de un sistema eutéctico en las mezclas de PO y PKO, principalmente en las proporciones 80/20, 60/40 y 50/50, demostrado por los diagramas de isosólidos y de isoconsistencia. La incompatibilidad entre los aceites disminuyó después de la interesterificación y la plasticidad de las mezclas mejoró, hecho demostrado por el incremento del contenido de sólidos y del límite de fluidez a temperatura ambiente.

PALABRAS-CLAVE: Aceite de palma - Aceite de palmiste – Consistencia - Contenido de grasa sólida - Interesterificación química.

SUMMARY

Interactions in interesterified palm and palm kernel oils mixtures. I-Solid fat content and consistency.

Palm oil (PO) and palm kernel oil (PKO) compositions (100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100) were interesterified in laboratory scale under predetermined conditions (0.4% sodium metoxide, 20 minutes, 100°C). The fourteen samples, before and after interesterification, were characterized by solid fat content (SFC) and consistency. Results showed a presence of eutectic system at PO and PKO compositions, mainly at 80/20, 60/40 and 50/50 fractions, proved through isosolids and isoconsistency diagrams. The incompatibility among the oils was decreased after reaction and improved the composition plasticity, demonstrated by the increment of solids value and yield value at room temperature.

KEY-WORDS: Chemical interesterification - Consistency - Solid fat content - Palm kernel oil - Palm oil.

1. INTRODUCTION

The chemical interesterification is an important tool to modify the compositions of fats and oils. The performance of final product of hydrogenated oils and fats is due the physical alterations in the fatty acids (trans isomers). The interesterification does not modify the profile of the starting raw material. The modifications in the melting and solidification properties of interesterified oils and fats are due to relative proportions of acylglyceride components after fatty acids re-arrangement (Erickson, 1995).

The interesterification is frequently confirmed through color monitoring, melting point and solid fat profile. The fastest techniques to control are the monitoring of brown color and melting point, but only when melting point alterations exists. The development of brown color is only a tool to verify the reaction, but the complete re-arrangement is dependent of many factors, like catalyst choice, reaction temperature, oil quality (Laning, 1985, Gioielli and Barufaldi, 1988, Erickson, 1995).

The solids profile is the main tool to the specification of fats used in margarine and fat products. The reading must be done at 4 temperatures at least, like 10, 20, 30 and 35°C or like 20, 30, 35 and 40°C (Young, 1985).

The crystals amount in oil mixtures, determined by solid fat content, is responsible for many characteristics of the products, that include general appearance, organoleptic properties, spread facilities and oil exudation (Lida and Ali, 1998).

The solid fat content between 4°C and 10°C determines the spread facilities of the product at refrigeration temperature. The solids content at up to 32% at 10°C, is essential to guarantee good performance of spread at refrigeration temperature (Lida and Ali, 1998).

The solid fat content between 20 and 22°C determines the product stability and its resistance against oil exudation. The ideal solid contents must be at least 10%. Between 35 and 37°C it determines the softness and smell properties in the mouth (Lida and Ali, 1998).

The solid profile has a good relation with hardness characteristics of plastic fats and contributes with the structure of final product (Woerfel, 1995).

Shortenings with small solid variation in a wide temperature range are defined as plastic fats. This plasticity is desirable in many products, as margarines and chocolates and can be used under several temperatures where aeration and crystalline structure at high temperatures are important. The plasticity range is less important in products used under controlled conditions or in melting state, like in frying (Woerfel,1995).

In some systems that contain fats, it is desirable a high solid content to promote an adequate crystalline structure in foods with a high content of fats, like margarines and chocolate under room temperature and low solid content in high temperatures, to promote an easy melting in the mouth (Woerfel,1995).

By definition, texture is a hardness measure of a product in a specified temperature. The consistency variation in a temperature range is defined as plasticity (Erickson, 1995). Texture, measured as consistency or plasticity, is one of the most important characteristics of fat products and is primarily determined through physical properties of fats and oils (Lida and Ali, 1998).

In margarines, texture appears as a very important parameter, because these products should have good spread properties under refrigeration and do not settle oils when leaved under room temperatures (Deman *et al.*, 1991).

Texture and spreadability depends on two main factors, that include a solid fat content and process conditions during the cooling and crystallization of emulsion (List *et al.*, 1995). The yield value parameter was described by (Haighton, 1959), and is considered as an independent parameter. The yield value is used to compare the several hardness index, obtained by penetrometers and other reological instruments.

The yield values in commercial margarines that were produced with hydrogenated soybean oil or mixtures of liquid and hydrogenated oils showed values from 200 $g.cm^{-1}$ for soft products until 2800 $g.cm^{-1}$ for hard products (List *et al.*, 1995).

The values that influence yield value and must be considered are: softness and cone format, structural hardness, penetration time and kinetic energy of the cone (Haighton, 1959).

2. EXPERIMENTAL

2.1. Material

Refined palm oil (PO) and palm kernel oil (PKO), supplied by Companhia Refinadora da Amazônia (CRA), Brazil.

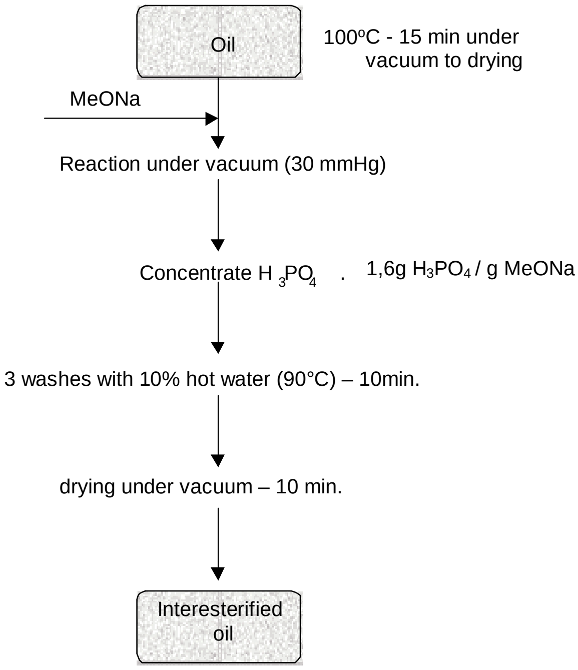

Figure 1
Chemical interesterification reaction scheme.

PO/PKO mixtures (%) – 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, 0/100 before and after interesterification reaction in the following conditions: 0.4% MeONa, 100°C, 20 minutes. (Figure 1).

Sodium methoxide, supplied by BASF S.A.

2.2. Methods

Free fatty acids – Method AOCS Ca 5a-40 (96)

Moisture and Volatile Matter – Method AOCS Ca 2c-25 (96)

Peroxide Value – Method AOCS Cd 8-53 (96)

Soap – Method AOCS Cc 17-79 (96)

Fatty acid composition – Method AOCS Ce 1c-89 (96)

Esterification – Method Hartman & Lago (1973).

Analysis conditions: Perkin Elmer Sigma 3B Chromatograph

Operation conditions:

Capillary column – fused silica CP-Sil-88, 50m x 0,25mm id., 0,2 μm film (Crompack). Oven temperature - 180°C –15 min., 180-200°C – 1°C / min; 200°C – 10 min; Detector: 300°C; injector: 270°C; Carrier gas (He) – 0.98 mL/min; Split -1:115.

Solid Fat Content: pNMR technique Minispec Bruker PC 120. Method AOCS Cd 16b-93 (1996). Serial procedure.

Texture: Texture Analyzer TA-XT2 (Stable Micro Systems), controlled by computer. The compression values were converted to yield value, in accord to Haighton (1959).

Sample preparation: the fats were melted and tempered during 24 hours at reading temperature (10, 20, 25, 30 and 35°C).

3. RESULTS AND DISCUSSION

The normal solid profile behavior after chemical interesterification reaction between palm and palm kernel mixtures showed a consistency increase to samples with a high palm oil content and a consistency decreased to palm kernel oil (Laning, 1985). Allen (1996) cited that normally the interesterification is accomplished with a mixture of two oils and for some products that require a high consistency they can absorb in their formulation hydrogenated oils. Chemical specifications of raw materials and solid fat content of PO/PKO mixtures before and after interesterification can be visualized at Tables I and II.

The composition that contain up to 60% of PKO showed a consistency increase. In other fractions, with 80 and 100% of PKO, the solid profile was lower. The desirable product must contain an intermediate solid content in a wide temperature range. The interesterification modify some melting properties and influence the velocity and morphology of crystals formation (Laning, 1985).

Palm kernel oil interesterified with small proportions of palm oil can be used in the preparation of coatings with good texture, without fragility at room temperature and with good melting properties (Goh, 1994).

Table I

Analytical characteristics and fatty acid composition of palm (PO) and palm kernel oils (PKO)

Characteristics		PO	PKO
Moisture and volatile matter(%)		0.04	0.04
Free fatty acids (% as palmitic acid to PO and % as lauric acid to PKO)		0.08	0.06
Peroxide value (meq O_2/Kg sample)		0	0
Soap (mg/Kg)		0	0
Fatty acid		**PO**	**PKO**
C8:0	Caprylic	—	4.9
C10:0	Capric	—	4.0
C12:0	Lauric	1.1	45.8
C14:0	Myristic	1.0	15.1
C16:0	Palmitic	40.7	9.2
C18:0	Stearic	5.0	2.4
C18:1	Oleic	42.0	16.1
C18:2	Linoleic	10.2	2.5

Table II

Solid fat content (%) of PO/PKO mixtures before and after interesterification

Before interesterification							
°C	100/0	80/20	60/40	50/50	40/60	20/80	0/100
10	36.02	33.44	38.19	43.85	47.16	55.95	61.9
20	13.08	9.23	8.34	14.44	17.23	27.41	37.1
25	10.07	7.69	4.61	3.52	3.88	8.64	16.82
30	6.95	5.32	2.49	2.3	1.45	0	0
35	3.3	2.2	0.66	0.19	0		
40	1.62	0	0	0			
45	0						
After interesterification							
°C	100/0	80/20	60/40	50/50	40/60	20/80	0/100
10	39.69	38.05	38.21	42.43	44.82	51.98	59.06
20	19.45	18.62	17.4	19.19	19.19	23.19	26.87
25	16.16	14.74	10.89	10.67	9.74	7.69	7.12
30	13.41	9.25	4.85	3.11	2.16	0.17	0
35	7.03	3.71	0.22	0	0	0	
40	3.79	0	0				
45	1.08						

Mean of standard deviations observed at each temperature - ± 0.2 (solid fat content value).

Figures 2 and 3 show isosolid diagrams of palm and palm kernel oils compositions before and after interesterification. (Lefebvre, 1983) cited that isosolids curves can be used to prove an eutectic system in oil mixtures. These diagrams represent under constant temperature, the solid content of several PO/PKO compositions (Rousseau *et al.*, 1996).

The behavior alteration in an isosolid profiles before and after interesterification characterizes the eutectic system formation. (Balbo and Gioielli, 1991) demonstrate that an efficient way to visualize an eutectic system is the depression curve, that was minimized after interesterification. (Young, 1985) cited that this softness effect can be useful in some cases, like in margarines obtained with palm and palm kernel oils mixtures. By the other side, the incompatibility between cocoa butter and substitutes promotes structure crystalline modification and softness of chocolate during the storage (Lannes and Gioielli, 1995).

The texture values, represented by yield value showed similar behavior that solid profiles. The consistency improve was noted at 40/60 fraction after interesterification and at 25°C a high consistency improvement was detected, that contributes to a better plasticity.

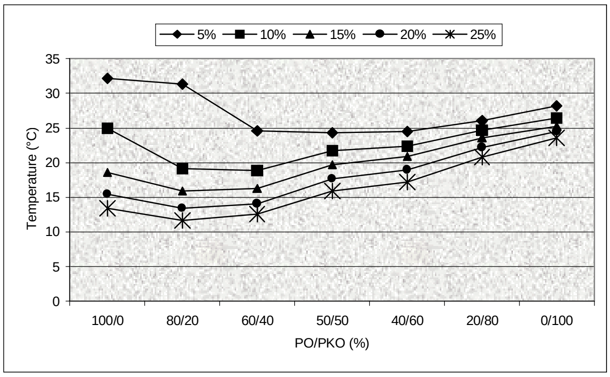

Figure 2
Isosolid curves of binary mixtures of PO/PKO before interesterification.

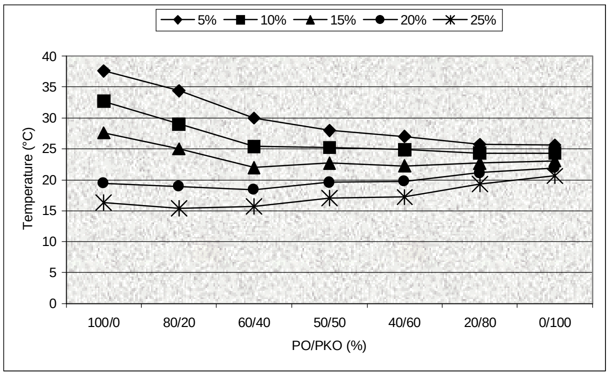

Figure 3
Isosolid curves of binary mixtures of PO/PKO after interesterification.

The eutectic effect was proved through yield values. This effect can be best visualized by consistency decreased at 20°C of the samples before interesterification at 80/20, 60/40 and 50/50 fractions. The Table III shows the yield values obtained for PO/PKO fractions.

The isoconsistency curve (Figures 4 and 5) is another way to visualize this effect.

The linearity absence at the evaluated range is cited as an important aspect to identify eutectic system. To the mixture of two components, (Hare, 1974) describes a mathematical model based on quadratic answer to solid fat index (SFI) values and that the factors are dependent, contrary to factorial experimental, where one of the factors can be varied independently.

The increase of linearity, observed at 80/20 and 60/40 fractions, after interesterification is an evidence that the technological process decreased the incompatibility and that this mixtures can reach more industrial applications than the original ones.

Table III
Yield value ($g.cm^{-1}$) of PO/PKO mixtures before and after interesterification.

°C	100/0	80/20	60/40	50/50	40/60	20/80	0/100
Before interesterification							
10	8740.8	8522.9	10454.9	12541.1	10561.6	13780.7	10481.6
20	1027.5	449.3	489.3	1090.3	1926.1	3902.6	6743.5
25	146.8	130.5	28.2	31.1	89	269.9	1118
30	0	0	0	0	0	0	0
After interesterification							
10	9093.7	7363.3	8634.1	9712	10204.3	8946.2	16316.2
20	1206.9	2281.9	3058.9	2769.8	3635.7	2670.4	4307.4
25	579.8	587.2	793.3	591.6	444.8	315.8	283.2
30	143.8	115.7	94.9	51.9	111.2	0	0
35	71.2	0	40	0	0		

Mean of standard deviations observed at each temperature - ± 6% (yield value content).

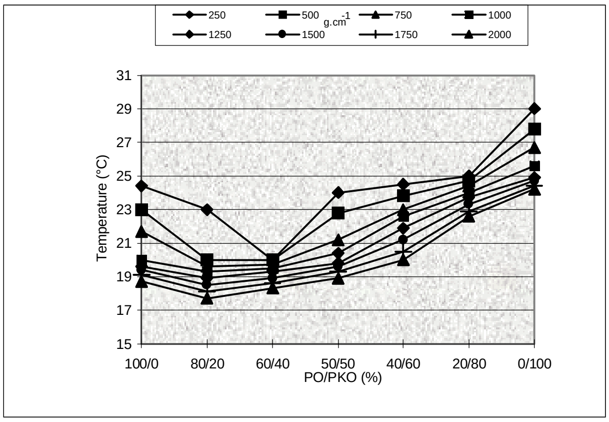

Figure 4
Isoconsistency curves of binary mixtures of PO/PKO before interesterification.

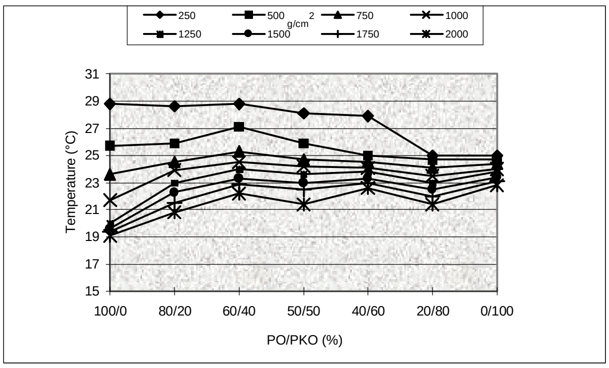

Figure 5
Isoconsistency curves of binary mixtures of PO/PKO after interesterification.

The Tables IV and V present the mathematical models of interactions to mixtures between two components and their correlation, according to (Hare, 1974).

The mathematical model, calculated by multiple regression for two components, according to (Hare, 1974) is the following:

$$Y = \beta_1 X_1 + \beta_2 X_2 + \beta_{1.2} X_1.X_2$$

Where Y is the estimated solid fat content or yield value, X_1 is palm oil proportion, X_2 is palm kernel oil proportion. $X_2 + X_1 = 100$. The R^2 is used to estimate the adjustment of the mathematical model for the to obtained data.

The statistics evaluation, with high correlation values (R^2) evidenced the perfect adjustment of mathematical model for the obtained data. To solid fat content at 20 and 25°C, the decrease of $\beta_{1.2}$ values is an indication that the reaction contributed to decrease the incompatibility.

Table IV

Interactions between PO/PKO mixtures before interesterification. Solid fat content (SFC) and «yield value» values

	Coefficients			
SFC	β_1	β_2	β_{12}	R^2
10°C	34.14	63.55	-24.20	0.99837
20°C	12.18	38.40	-47.83	0.99446
25°C	11.11	16.24	-38.57	0.98867
Yield Value	β_1	β_2	β_{12}	R^2
10°C	7.95×10^3	1.15×10^4	6.80×10^3	0.98833
20°C	1.02×10^3	6.79×10^3	-1.11×10^4	0.99926
25°C	239.47	1.00×10^3	-2.41×10^3	0.94166

Table V

Interactions between PO/PKO mixtures after interesterification. Solid fat content (SFC) and «yield value» values

	Coefficients			
SFC	β_1	β_2	β_{12}	R^2
10°C	39.13	59.88	-30.76	0.99955
20°C	19.57	27.08	-18.46	0.99946
25°C	16.55	6.90	- 4.82	0.99827
Yield Value	β_1	β_2	β_{12}	R^2
10°C	9.07×10^3	1.51×10^4	-1.37×10^4	0.98474
20°C	1.40×10^3	3.87×10^3	1.43×10^3	0.97679
25°C	597.25	219.30	702.65	0.97262

4. CONCLUSION

Palm and palm kernel fractions showed characteristics of eutectic system, mainly at 80/20 and 50/50 PO/PKO fractions. The chemical interesterification at 100°C and 20 minutes with 0,4% of sodium methoxide minimized the incompatibility between the fractions and improved the plasticity.

The use of binary systems PO/PKO after interesterification, mainly in levels of 20 – 50% of PKO, showed a great promise in terms of industrial process at products with a low isomers trans content. The results obtained can be compare with characterization done by (Grimaldi, *et al.,* 2000) with commercial shortenings. These mixtures could be used like ingredients for bakery products and ice cream that exhibit similar melting profiles with the advantage that contain a low trans isomers content in their formulation.

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